



Liquid transport through sulfonated cation-exchange membranes for different water–alcohol solutions

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ABSTRACT

The aim of this work was to study the sorption and transport of different water–alcohol solutions (methanol, ethanol, 1-propanol and 2-propanol solutions) when a Nafion 117 membrane is separating them. It was observed that methanol permeability remains constant when varying the composition of the mixture. However, the permeability for the other alcohol solutions decreases from alcohol concentrations that are different for each alcohol. In addition, it was aimed to compare the behavior of membranes with different morphologies when they were separating water and water–alcohol solutions. Nafion 117 membrane and two sulfonated cation-exchange membranes (CR65-AZL-412 and MK-40) were used. Measurements of sorption and liquid transport were made using methanol and ethanol solutions. The uptake values for Nafion 117 membrane were higher than those obtained for CR65-AZL-412 and MK-40 membranes. The results reveal that, in contrast to Nafion membrane, a non-negligible water flux through CR65-AZL-412 and MK-40 membranes was observed along with the alcohol diffusion through them. For these two latter membranes the permeability could not be calculated since the alcohol diffusion is not the only physical process that should be considered. In spite of it, the alcohol and water fluxes through CR65-AZL-412 and MK-40 were estimated; turning out that the water flux was higher than alcohol flux.

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1. Introduction

One of the most used ion-exchange membranes in analytical chemistry and in industry is Nafion membrane. The wide-ranging applications of this membrane are due to its excellent properties, as can be good water ion exchange, high electrical conductivity, excellent thermal and chemical stability and low gas permeability. Attending to these properties, Nafion membrane has one of its main uses in direct methanol fuel cell (DMFC), where it is commonly used as electrolyte. DMFC is hindered by methanol diffusion from anode to cathode side through the polymer electrolyte membrane [1–5], but this is not the only difficulty that has been found but also the slow kinetic of the oxidation reaction of methanol at the anode [6]. To overcome these problems some different solutions have been proposed. One of the solutions has been to replace methanol by other alcohols, mainly ethanol [7,8]. Although direct ethanol fuel cells (DEFCs) present some advantages over DMFC, higher energy density and non-toxicity, the diffusion of the alcohol through the membrane is not avoided. It seems clear that the understanding of the alcohol crossover through the membrane should be one of the major issues at the study of Nafion 117. This is one of the aims of the present work. To address

it, we study the sorption and the permeation characteristics of different alcohols when a Nafion membrane is separating water and water–alcohol solutions. They have been using methanol and ethanol water solutions because they are the most employed with the Nafion membrane. But they have been also added 1-propanol and 2-propanol solutions to the study because their physical and chemical properties are different enough to those of methanol and ethanol solutions and have been less used with this membrane.

Not only Nafion but also other ion-exchange membranes are extensively used in an important number of processes in chemical and biochemical industry. Up to now, these transport processes in ion-exchange membranes were mainly developed in aqueous media. However the use of this kind of membranes in hydro-organic media allows the opening of new and important applications, which demand the development of new ion-exchange membrane solving the important technical and commercial limitations of the current ion-exchange membranes [9–12]. This is an important research domain, which involves the study of the influence of the membrane morphology in the transport coefficient in this kind of media. The membranes can be classified attending to different aspects, one of them is their structure. According to this aspect, ion-exchange membranes are divided into two major categories, the first one comprises homogeneous membranes that are polymers with ion-exchange groups bound to the polymer backbone. The second one consists of heterogeneous membranes that are neutral

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Table 1
Membranes characteristics: thickness (Th), maximum water uptake (MWU) and ion-exchange capacity (IEC).

	Th (μm)	MWU (%)	IEC (mequiv./g)
Nafion 117	183	35	0.941
MK-40	510	40	2.60
CR65-ALZ-412	570	43	2.1

polymer matrices randomly filled with micron size ion-exchange particles.

The structural differences are responsible for different behaviors under the same conditions. In a previous paper [13] liquid uptake and permeation fluxes as a function of the applied pressure difference were reported. It was obtained that both, the liquid uptake and the permeation show an important dependence on the structure of the ion-exchange membrane. In order to achieve a better understanding of the influence of the membrane morphology on the factors controlling sorption and permeability, different cation-exchange membranes separating water and water–alcohol solutions have been investigated. Two different alcohols, methanol and ethanol, and three sulfonated cation-exchange membranes of different structures have been selected. Nafion 117 is chosen as its significant use for direct fuel cell, and CR65-ALZ-412 and MK-40 as being reference membranes for electro dialysis.

2. Experimental part

2.1. Membranes and materials

The first kind of membrane used was a Nafion 117 (Nafion) produced by Dupont Inc., and its nominal equivalent weight is 1.1 kg/equiv. Prior to testing, the Nafion membrane was introduced in a 0.25 M HCl solution during 48 h, at room temperature, for its complete conversion to an H⁺ form. Then, the membrane was washed with deionized bidistilled water. The properties and morphology of Nafion membrane have been at length studied in the literature [14,15]. Based on these studies, it is known that the membrane consists of a matrix (polytetrafluoroethylene backbone) and regularly spaced perfluorovinylether side chains ending in sulfonic acid groups. It has been proposed that the membrane would be understood as hydrophilic areas made up of the sulfonic acid groups clustered in spherical domains (4–5 nm) connected by channels to a hydrophobic perfluorocarbon matrix.

The cation-exchange membrane MK-40 (MK40) produced by OAO ShchekinoAzort is a heterogeneous membrane with sulfonic groups as fix sites. According to the data provided by the manufacturer, the cross-linking degree of the membrane is 8%. This membrane was used as received without any previous treatment. In accordance with the literature [16], these membranes consist of ion-exchange particles (sulfonated groups chemically attached to polystyrene/divinylbenzene copolymer chains) dispersed in the polymer matrix. The membrane surface areas corresponding to the exit of ion-exchange resin particles have linear dimensions within the range from 10 to 30 μm .

CR65-ALZ-412 membrane (CR65) produced by Ionics Inc. is a type web supported styrene-divinylbenzene (DVB)-based membrane with sulfonic acid functional groups. In the membrane manufacture, styrene and DVB are copolymerized using an initiator (BPO) to get a homogeneous viscous polymer solution. Attending to the data provided by the manufacturer, the membrane is mainly hydrophilic. CR65 was used without any previous treatment.

The thickness, maximum water uptake and ion-exchange capacity, given for the manufacturer, for the three membranes are shown in Table 1.

Table 2
Physical and chemical properties of water, methanol, ethanol, 1-propanol and 2-propanol at 25 °C and 10⁵ Pa. Density (ρ), viscosity (μ) and molar mass (M).

	ρ (g/cm ³)	μ (mPa s)	M (g/mol)
Water	0.9970	0.890	18
Methanol	0.7865	0.541	32
Ethanol	0.810	1.0774	46
1-Propanol	0.799	1.938	60
2-Propanol	0.781	2.070	60

Pure pro-analysis grade methanol, ethanol, 1-propanol, 2-propanol (Panreac) and bidistilled pure water were used in this work. Their main physico-chemical characteristics are given in Table 2 [17].

2.2. Determination of liquid uptake in the membrane

In order to determine the water–alcohol solution uptake, a sorption study with Nafion membrane was performed by using aqueous mixtures of methanol, ethanol, 1-propanol and 2-propanol at different concentrations. The study was made using aqueous methanol and ethanol solutions for the two other membranes (MK40 and CR65). In this case, the investigation was not extended to 1-propanol and 2-propanol since at the permeability study these alcohols were not employed.

Before the experiments, the membrane samples were dried in a vacuum oven at 100 °C during 24 h. After that, the samples were weighed and then immersed in a close bottle containing a known mass of the corresponding solution and allowed to equilibrate at room temperature. After 48 h of immersion, the swollen membranes were taken out of the solution, dried with filter paper and weighed again. The liquid uptake degree, S , was calculated according to the following formula:

$$S = \frac{m_w - m_d}{m_d} \quad (1)$$

where m_w and m_d are the masses of the swollen (dried with filter paper) and dry membrane (dried in a vacuum oven), respectively.

The density of the solution in the bottle, before and after membrane immersion, was measured in order to estimate whether a component of the solution, water or alcohol, is preferentially sorbed by the membrane. It was obtained that the results were reproducible for all the membrane at any alcohol concentration.

2.3. Concentration change measurements

The experimental device is only briefly summarized here, since it is similar to the ones used in previous works [18–20]. Basically, the membrane was housed at a PTFE cell, consisting of two independent chambers with an approximate volume of 10^{-4} m^3 , the active membrane area was $25.3 \times 10^{-4} \text{ m}^2$. Two glass reservoirs of capacity of $0.5 \times 10^{-3} \text{ m}^3$ were employed to contain the circulating solution in both chambers. Both, in the cell and in the glass reservoir, temperature probes were introduced in order to control the temperature inside and outside the chamber. The solutions were circulated between the cell and the reservoirs by means of a peristaltic pump (Masterflex L/S model, Cole-Parmer).

Water was introduced in one reservoir and the water–alcohol solution in the other one. When a temperature of 25 °C is achieved in both chambers, the solutions were circulated through the cell. The chamber that contained pure water was placed over a mass balance (Sartorius BL3100 model) so the mass changes as a function of the time could be measured. The accuracy in the mass measurements was $\pm 10^{-4} \text{ kg}$.

The density of the water–alcohol solution was measured in the reservoir at the beginning and every hour during the exper-

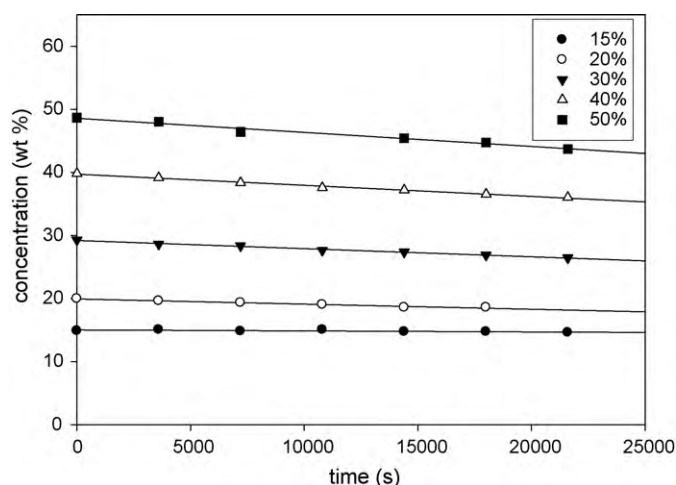


Fig. 1. Change in methanol concentration in the concentrated chamber with time in Nafion membrane for the methanol–water solutions with different composition.

iment. The density of the reservoir that initially contained water was measured at the beginning and at the end of the experiment. The temperature of these samples was led to 20 °C and then the density measurements were made using an AP Paar Density Meter, model DMA58, with an accuracy of $\pm 10^{-2} \text{ kg m}^{-3}$. As it is known, the density of a water–alcohol solution varies with its composition, for that reason, it is possible to estimate the corresponding alcohol concentration of the solution from the measured density values if the calibration curve of density–concentration is known. In this work, the calibration curve has been determined from the data found in the literature for alcohol–water solution densities dependence with the alcohol concentration in mixtures at 20 °C [21]. Using these curves, the alcohol concentration in the concentrated chamber, which initially contained the alcohol–water mixture, was determined as a function of the time. Once the steady state conditions were reached, the values were fitted to a straight line, whose slope let us to calculate the concentration change rate. As an example, an illustrative plot is shown in Fig. 1, corresponding to a Nafion membrane which is separating water and methanol–water solutions with different initial methanol concentrations.

The alcohol permeability was obtained in accordance with Fick's law equation for diaphragm-cell diffusion. Some assumptions should be made in order to apply the diagram-cell equation [22]: (1) The concentration polarization may be neglected when the solution is circulated between the cell and the reservoirs at both sides of the membrane. (2) The difference of concentrations is responsible for the alcohol flux across the membrane. (3) After an initial transient, the steady state conditions are reached since the volume of the solutions is big enough in comparison with the membrane volume. (4) The flux across the membrane achieves a pseudo-steady state in a very short period of time.

Bearing these assumptions in mind, the alcohol permeability was obtained by using the following relationship [6]:

$$P = \frac{dC_{al}}{dt} \frac{V_{al}L}{A(C_w - C_{al})} \quad (2)$$

where C_{al} is the alcohol concentration in the concentrated solution and C_w the alcohol concentration in the diluted solution, L the membrane thickness, A is the active membrane area and V_{al} is the concentrated solution volume.

2.3.1. Determination of alcohol and water flux

The mass change in the diluted chamber, when the membrane separated two alcohol–water solutions was measured as a function of time. After a period of time, a linear relationship was found

Table 3

Total liquid uptake by Nafion membrane as a function of the alcohol concentration in aqueous methanol, ethanol, 1-propanol and 2-propanol mixtures.

Alcohol (wt%)	Methanol	Ethanol	1-Propanol	2-Propanol
10	0.36	0.44	0.85	0.81
20	0.40	0.94	1.54	1.56
30	0.45	1.08	1.96	2.00
40	0.52	1.68	2.18	2.50
50	0.64	1.79	2.24	2.37

that permitted us to obtain the total mass flux β from the slope of the corresponding straight line. This mass flux was due to two contributions, alcohols flux, for diffusion, and water flux, for osmosis. During each experiment, also the alcohol concentration in the concentration chamber was also determined as a function of time. A linear dependence between alcohol concentration and time was found in all cases. Again, the linear dependence permitted us to obtain the concentration change velocity, α from the slope of the corresponding straight line.

The individual fluxes of alcohol and water through the membrane were estimated using data of α , β and the initial mass in the concentrated chamber. The method to determine the alcohol and water flux through a membrane is similar to that described in a previous work [20]. The alcohol J_a and water J_w , fluxes were obtained by means of the following expressions:

$$J_a = \frac{1}{100A}(c_c^0\beta + \alpha m_c^0) \quad (3)$$

$$J_w = \frac{1}{100A}(100\beta - c_c^0\beta - \alpha m_c^0) \quad (4)$$

where c_c^0 and m_c^0 are the initial concentration and initial mass, respectively, in the concentrated reservoir.

3. Results and discussion

3.1. Liquid uptake in the membrane

The liquid uptake values of the different alcohol solutions by a Nafion membrane are shown in Table 3. The measure error was always lower than 5% for the four alcohols. It is observed that the liquid uptake for the different aqueous solutions increase in the sequence: methanol < ethanol < 1-propanol \leq 2-propanol. The results seem to indicate that the liquid uptake by the membrane is dependent, to a certain extent, to the viscosity of the solutions, because the higher the solution viscosity, the higher the liquid uptake. This effect may be caused by the formation of associates of alcohol molecules with water molecules and with fixed groups in the Nafion membrane. The formation of aggregates would be more significant for alcohols with the higher viscosity. The results are in agreement with those reported by other authors [14,23]. The analysis of the variation of the composition of the water–alcohol mixtures reveals that the alcohol uptake, in each case, by the membrane is slightly larger than water uptake, however, the changes are not significant. The higher sorption of alcohol compared to water, could be explained attending to Nafion structure [24–26]. It is known that some hydrophobic–hydrophilic separation appears when the Nafion membrane comes into contact with a polar solvent. Thus, water molecules are only at hydrophilic domains, while the alcohol molecules can also be at certain extent in the hydrophobic fluorocarbon backbone.

For all the alcohol solutions, a significant increase of liquid uptake is found when the alcohol content of the solution rises. This behavior could be explained by the increase in wet membrane porosity, which brings about the rising of the mobility of solvents in membrane, beside the increase of the mobility of the polymer pendant chain. An exception is the 2-propanol solution where the

Table 4

Total liquid uptake by CR65 and MK40 membranes as a function of the alcohol concentration in aqueous methanol and ethanol mixtures.

Water–methanol					
Alcohol (wt%)	10	20	30	40	50
CR65	0.44	0.49	0.51	0.54	0.55
MK-40	0.49	0.45	0.43	0.42	0.44
Water–ethanol					
Alcohol (wt%)	10	20	30	40	50
CR65	0.60	0.63	0.64	0.64	0.62
MK-40	0.47	0.46	0.43	0.45	0.43

uptake values decrease at high alcohol concentration values. A similar behavior is also found to 2-propanol by Saarinen et al. [27] with Nafion 117 membranes. It is known that the particles interact each other forming associations and our results suggest that at high enough alcohol concentration (that is the case for 2-propanol at 50% concentration) these associations could be bigger than the pores of the membrane that are blocking the entrance to the polymer matrix. This decrease could be also due to the confidence interval of the measurement of the liquid uptake, which makes that the obtained values for 40% and 50% 2-propanol solutions appear to be different when in fact they are similar. In this case, there would not be a decrease but it would reach an asymptotic value.

The obtained results for the other two membranes are shown in Table 4. Unlike Nafion membrane, the dependence of CR65 and MK40 liquid uptake with the alcohol concentration results to be not very important. Except in the low alcohol concentration range, the uptake values are lower for CR65 and MK-40 membranes than for Nafion, specially in the case of ethanol solutions. This could be explained because these membranes have a very low polymer matrix swelling in water and alcohols [27–29], for that reason, the amount of liquid within the membrane is determined by the degree of swelling of the ion-exchange particles. It is also found that CR65 sorption values are slightly higher than those of MK40. For CR65 membrane, a small increase of the liquid uptake is observed with alcohol concentration, both aqueous methanol as ethanol mixtures. It should be also noted that the density variation of the solution in the bottle, before and after CR65 membrane immersion, was too small and within experimental accuracy. This means that neither water nor alcohol was preferentially taken by this membrane. On the other hand, for the two alcohol solutions studied, the MK40 membrane liquid uptake seems to be independent of alcohol concentration. Moreover, the analysis of the composition of the water–methanol and water–ethanol solutions reveals that the water uptake was slightly larger than that of alcohol. However, the composition changes are too small to see a clear trend. This result may be understood remembering that when a polar solvent is taken, such as water and alcohols, the sorption depends on chemical polarity of the solvent. Due to its higher polarity, the water molecules interact more than alcohols molecules with the ion-exchange particles. Furthermore, the alcohol molecules are more difficult to accommodate in the sorption sites than water particles due to their greater molecular size. These could be the reasons why the water sorption is higher than that of alcohol for the MK-40 membrane.

3.2. Liquid transport

The values of the permeability were obtained for the different membrane systems as described in the experimental section. The alcohol permeability coefficients in Nafion membrane are presented in Fig. 2, as a function of the solution composition for the different mixtures studied. The results show a very different behavior depending on the alcohol type. The methanol permeability is practically independent of methanol content of the solution. The

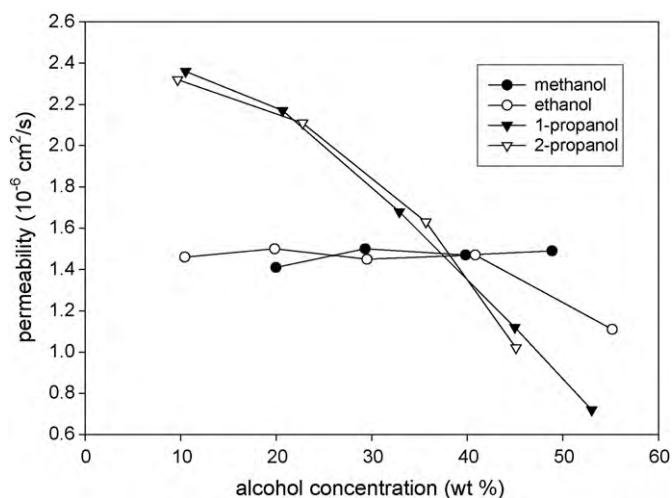


Fig. 2. Alcohol permeability coefficient through Nafion membrane as a function of the alcohol concentration for aqueous methanol, ethanol, 1-propanol and 2-propanol solutions. The solid lines are only visual guides to avoid confusion between various symbols.

1-propanol and 2-propanol permeability decreases significantly with its concentration from the lowest alcohol concentrations studied. For the ethanol case, the permeability values seem to be almost constant until an alcohol concentration of approximately 40% to decrease later. The obtained values for the methanol are in agreement with those found at the literature [5,30–32]. As it was said, Nafion is not-crosslinked membrane; therefore the size of ionic clusters and hydrophobic regions may vary according to the solvent [19]. This fact could account for the different behavior observed for the water–alcohol solutions. The permeability decrease of ethanol and propanol in the membrane may be explained by the existence of bulky associations that appear when a certain alcohol concentration is achieved. The bulk association degree would be explained attending to the viscosity coefficient value. Due to the larger values of the viscosity of 1-propanol and 2-propanol compared to that of water, as their concentration in the aqueous solutions is increased, the viscosity rises significantly. This means that the particles interact with other particles forming associations that would difficult the solution transport through the polymer matrix. In contrast, as the methanol viscosity is comparable or even smaller than that of water, such effect is not found in their aqueous solutions, which explains the constancy of the permeability of methanol over the composition range studied. At ethanol solution, the viscosity effects should be appreciated around 50% solution concentration when their values are high enough. For 1-propanol and 2-propanol the viscosity influence appears at any alcohol concentrations and its effects are so strong that the permeability undergoes a remarkable decrease. The 1-propanol and 2-propanol alcohols behavior is quite similar since their viscosities are very similar as well.

In accordance with Eq. (2), when the alcohol permeability is estimated, a negligible water flux through the membrane is assumed. This water flux is driven by an osmotic pressure difference across the membrane due to the different concentration of water in the diluted and concentrated reservoirs. This water flux would go from the diluted chamber (initially filled with pure water) to the concentrated chamber (initially filled with the water–alcohol solution at a given composition). For the Nafion membrane, there are experimental evidences showing that the water flux is negligible over the composition range studied [6,30,31], which makes that the above assumption is accepted, and the alcohol permeability can be calculated. In contrast, it was found a water flux through both CR65 and MK40 membranes, which was experimentally evidenced by a mass decrease of the liquid contained in the diluted chamber.

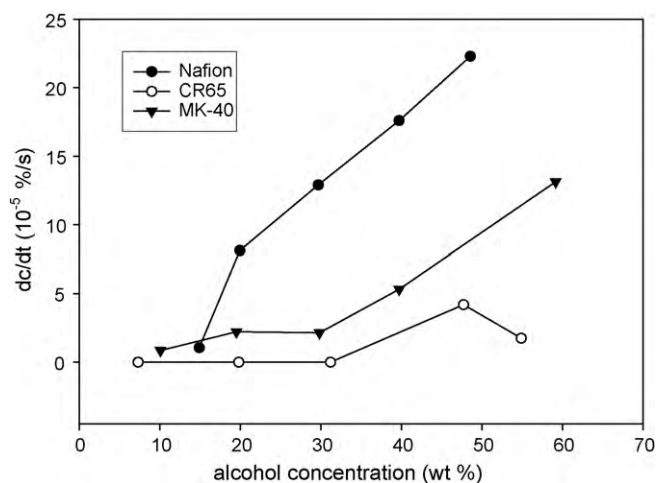


Fig. 3. Change in methanol concentration with time in the concentrated chamber as a function of the methanol concentration in water–methanol solutions for Nafion 117, CR65 and MK-40 membranes. The solid lines are only visual guides to avoid confusion between various symbols.

This fact is related to the much larger hydraulic permeability of these membranes compared to that of Nafion [13], because the osmotic pressure difference is the same in all cases. Consequently, in view of our experimental results, the approximation of negligible water flux implicit in Eq. (2) cannot be done for CR65 and MK40 membranes. This means that the alcohol diffusion is not the only physical process that is governing the liquid transport in the membrane, and the osmosis should be taken into consideration as well. In order to estimate qualitatively the alcohol diffusion through the membrane, the concentration change with time is represented in Figs. 3 and 4, for methanol and ethanol solutions, respectively. It must be indicated that the measurements are made at slightly different alcohol concentrations for the two membranes and also different than in the case of Nafion. This is due to the same initial concentration it is not always possible to keep. It is found that the alcohol diffusion process is more important in the Nafion membrane, because the temporal changes of the alcohol concentration values are significantly higher than those corresponding to the other two membranes, which is in agreement with the results obtained when the liquid uptake was estimated. Thus, at higher

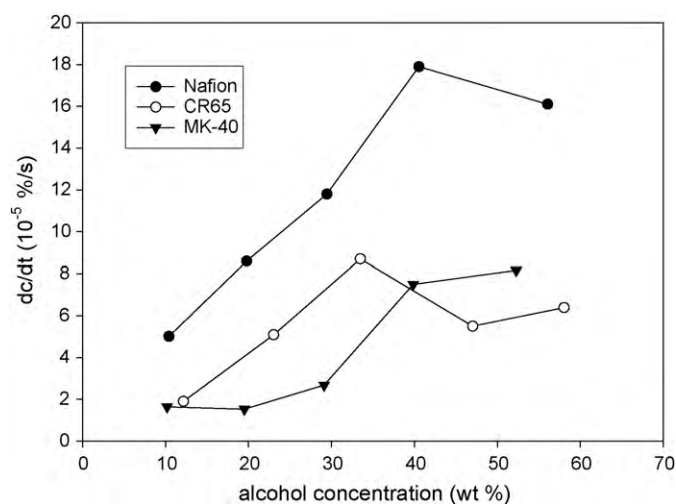


Fig. 4. Change in ethanol concentration with time in the concentrated chamber as a function of the ethanol concentration in water–ethanol solutions for Nafion 117, CR65 412 and MK-40 membranes. The solid lines are only visual guides to avoid confusion between various symbols.

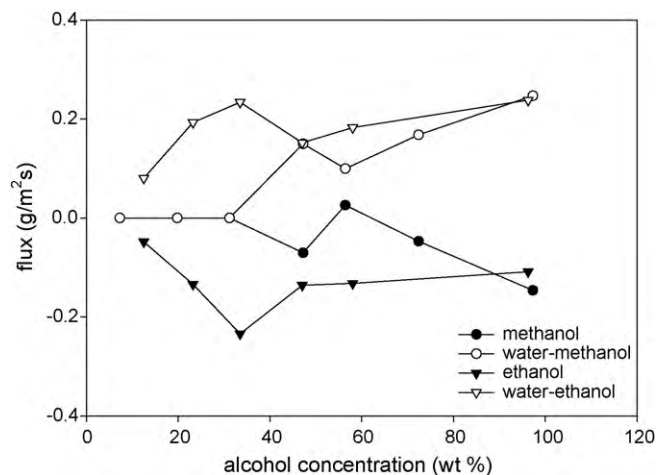


Fig. 5. Fluxes versus weight alcohol percentages for a CR65 membrane. (▼) Ethanol flux, when the membrane is separating water and ethanol solutions. (△) Water flux when the membrane is separating water and ethanol solutions. (●) Methanol flux, when the membrane is separating water and methanol solutions. (○) Water flux when the membrane is separating water and methanol solutions. The solid lines are only visual guides to avoid confusion between various symbols.

alcohol concentrations, Nafion becomes an even poorer alcohol barrier, while CR65 and MK-40 are better barriers at any concentration.

Although the alcohol permeability cannot be calculated for CR65 and MK40 membranes using Eq. (2), alternatively the alcohol and water fluxes through the membrane can be estimated using Eqs. (3) and (4). The results are shown in Figs. 5 and 6 for CR65 and MK40 membranes, respectively. At a given alcohol concentration in the solution, the water fluxes are slightly larger than alcohol fluxes for both membranes. This fact indicates that, although the alcohol diffusion through the membrane exists, the water osmosis is a bigger transport process, although it is not significant to extract any significant conclusions. It should be stressed that this is an important difference between these CR65 and MK40 membranes and Nafion, since the alcohol diffusion is the governing transport process in the last membrane. When the results obtained for CR65 and MK40 are compared major fluxes are found for the second one, in fact, at methanol concentration lower than 40% no transport process is

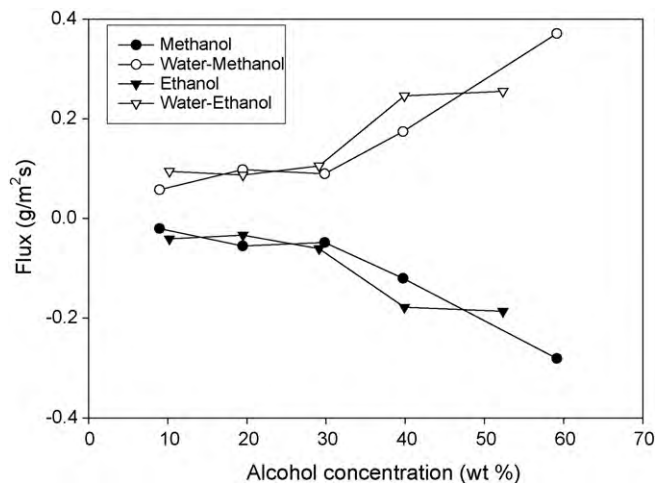


Fig. 6. Fluxes versus weight alcohol percentages for a MK-40 membrane. (▼) Ethanol flux, when the membrane is separating water and ethanol solutions. (△) Water flux when the membrane is separating water and ethanol solutions. (●) Methanol flux, when the membrane is separating water and methanol solutions. (○) Water flux when the membrane is separating water and methanol solutions. The solid lines are only visual guides to avoid confusion between various symbols.

observed for CR65 membrane, for that reason in Fig. 5 the water flux values are put on top methanol values.

4. Conclusions

From the contributions of this research we should emphasize two points. On the one hand, the use of a great number of alcohols simultaneously in order to analyze the uptake and permeability of Nafion membrane. On the other hand, it deserves to underline that there are no similar works concerning to the study of permeability and sorption parameters of 1-propanol and 2-propanol at Nafion 117.

For Nafion membrane, a significant increment of liquid uptake was found when the alcohol content of the solution increases. Moreover, it seemed that alcohol is preferentially taken by the membrane over water, for all the alcohol solutions. As a whole, the uptake values calculated for CR65 and MK40 membranes were lower than those obtained for Nafion. For CR65 a slow increase appeared when the alcohol concentration rises, also it was observed that neither water nor alcohol was preferentially uptaken by this membrane. The MK40 membrane measures seemed to indicate that liquid uptake was independent of alcohol concentration. For this membrane it was found that water uptake was slightly larger than that of alcohol.

Nafion permeability measures showed that the behavior of methanol solutions was different from the other alcohols. Whereas methanol permeability remains constant with the methanol content, for ethanol, the values are also independent of alcohol concentration until a given concentration is achieved. For ethanol concentrations higher than 40% the permeability decreases. At the other two alcohols, the permeability decreased at any alcohol concentration studied. The different alcohol behaviors were explained attending to associative effects. The particles could interact with other particles forming associations that would make difficult the solvent transport through the membrane. At CR645 and MK40 membranes the alcohol diffusion was not the only physical process that was governing the liquid transport through the membrane and the flux of water could not be neglected. The alcohol and water fluxes through the membrane could be obtained turning out that the water flux was always greater than alcohol flux. It could mean that the osmosis is more important than alcohol diffusion at those kinds of membranes.

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